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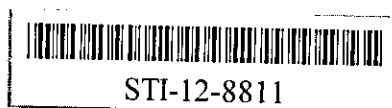
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# THE PHILIPPINE JOURNAL OF SCIENCE

A. CHEMICAL AND GEOLOGICAL SCIENCES  
AND THE INDUSTRIES

VOL. XI

JANUARY, 1916

No. 1

## NOTES ON THE WATER SUPPLY OF THE CITY OF MANILA<sup>1</sup>

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The object of this paper is to present some of the factors influencing the quality of the water used in supplying the city of Manila, with special reference to the disinfection of the water by means of choride of lime.

### THE MANILA WATER-SUPPLY SYSTEM

The construction of a water-supply system for the city of Manila was undertaken in 1878 by the municipality under the Spanish Government; the installation was first used by the public in 1882. The system derived its water from Mariquina River at Santolan, where a pumping station having a daily capacity of about 28,400 cubic meters (7,500,00 gallons) was installed. From the river the water was pumped to a "deposito," or reservoir, consisting of a series of underground chambers having a capacity of about 60,000 cubic meters (16,000,000 gallons); thence it was piped by gravity to the city distributing system. The total daily capacity of the installation was from 113 to 114 liters (30 gallons) per capita, on the basis of the estimated population of Manila.

As Mariquina River passes through a thickly populated area including a number of large towns before it reaches the Santolan pumping station, it was a difficult matter to keep the water uncontaminated; therefore, it was not long before it became necessary to look for a new source of supply of better quality, large enough to furnish the city of Manila and to provide for the natural increase in population.

Plans were accordingly drawn up in 1902 for a new supply system (completed in 1908) deriving its water from Mariquina River at a point above which it entered inhabited districts. A dam was constructed at Montalban Gorge about 25 kilometers

<sup>1</sup> Received for publication November 11, 1915.

(15.7 miles) from Manila, and the watershed above that point, about 1,550 square kilometers (60 square miles), was reserved from settlement. The minimum daily flow in the river during the dry season is estimated at 41,700 cubic meters (11,000,000 gallons). The storage capacity of the dam was estimated at something over 4,700,000 cubic meters (1,250,000,000 gallons), although this figure is not effective owing to leakage at the dam, a loss which fissures and cracks in the limestone composing the walls and floor of the gorge make more or less unavoidable. A new reservoir having a capacity of about 206,000 cubic meters (54,500,000 gallons) was constructed on high ground near the city.

With this arrangement Manila now has a complete gravity system, the water flowing from Montalban to the new reservoir, thence to the city distribution system. The consumption of water (October, 1915) is about 57,000 cubic meters (15,000,000 gallons) a day, corresponding to a per capita consumption of approximately 220 liters (58 gallons). At this rate the storage capacity of the new reservoir is about three and one-half days.

There are generally enough rains in the dry season to maintain a supply of water adequate for the city's needs, and if it were not for leakage at the dam, the supply would probably be sufficient; in periods of extended drought, however, it frequently happens that there is not sufficient water from Montalban to supply Manila. At such times it becomes necessary to augment the supply by using the old Santolan pumping station and the old deposito, whose capacity is now about 72,000 cubic meters (19,000,000 gallons). While the Santolan system is in operation, guards are placed along the banks of Mariquina River to prevent contamination of the water so far as possible.

The new supply system is a tremendous improvement over the old installation. The Bureau of Health<sup>2</sup> has pointed out that there were 300 per cent more deaths from intestinal diseases in the years just preceding the installation of the new supply system than in the years immediately following, and has shown<sup>3</sup> further that when the inadequacy of the Montalban supply made it necessary to resort to the old Santolan system to supplement the city supply a marked increase in the death rate occurred. At the time these observations were made, the water was used just as it came from Montalban, no attempt being made to purify it.

At the present time there is no provision made for filtration

<sup>2</sup> *Ann. Rep. P. I. Bur. Health* (1912), 5.

<sup>3</sup> *Ibid.*, 47.

or for any sedimentation except that naturally occurring at Montalban and at the reservoir. The only method of purification employed consists of the addition of chloride of lime to the water, just as it leaves the reservoir.

#### QUALITY OF THE WATER FROM MONTALBAN

Chemically the quality of the water from Montalban leaves little to be desired so far as its use for city supply is concerned. The water is moderately hard, usually slightly turbid, and has a low mineral content. Its turbidity is not great enough to be objectionable, but as it is due mainly to extremely fine particles of clay and silt, sedimentation is comparatively slow. As already pointed out by Bliss,<sup>4</sup> seasonal variations in the water are surprisingly slight, in spite of the heavy rains of the wet season, which greatly change the amount and appearance of the water coming from the watershed.

Typical analyses of the Manila water, coupled, for comparison, with older analyses of the Mariquina supply, are shown in Table I.

TABLE I.—Analyses of Manila water supply.

[Results expressed as parts per million.]

	1903 a		1906 b	1909 c	1913 c
	Mini- mum.	Maxi- mum.			
Total solids.....	153	220	215	157	154
Fixed solids.....	127	190		125	
Loss on ignition.....	16	46		32	
Silica (SiO <sub>2</sub> ).....			44.7		23.7
Oxides of iron and aluminium.....					1.7
Calcium (Ca).....			16.4		31.2
Magnesium (Mg).....			5.4		6.5
Sodium (Na).....			8		12.7
Potassium (K).....			2.3		1.9
Normal carbonates (as CO <sub>2</sub> ).....					0
Bicarbonates (as CO <sub>2</sub> ).....					139
Sulphates (SO <sub>4</sub> ).....			18.7		13.8
Nitrates (N).....	trace	0.36		0.02	0.046
Nitrites (N).....	0	trace		trace	trace
Free ammonia (N).....	0	0.036		0.12	0.03
Albuminoid ammonia.....	0.031	0.100		0.1	0.116
Oxygen consumed.....	0.65	2.20		1.65	
Total hardness (as CaCO <sub>3</sub> ).....	58.8	109	99	90	
Chlorine (Cl).....	2.1	4.4	3.9	3.1	4.1

<sup>a</sup> Analysis by C. H. Bliss, chemist, Bureau of Science.

<sup>b</sup> Analysis by L. A. Salinger, chemist, Bureau of Science.

<sup>c</sup> Analysis by V. Q. Gana, chemist, Bureau of Science.

<sup>4</sup> *Pub. P. I. Bur. Govt. Lab.* (1905), No. 20, 10.

The constancy in quality is further indicated by the chlorine content and oxygen-consuming capacity of the water in the reservoir, as shown by determinations made during the rainy season, at a time when the greatest variation in quality might reasonably have been expected.

Chlorine was determined by Mohr's method. The oxygen-consuming capacity was measured by the method designated as standard by the American Public Health Association,<sup>5</sup> except that the sample was acidulated and heated to boiling before the addition of the permanganate, and that the digestion was made on a steam bath instead of in a bath of boiling water.

TABLE II.—Daily variation in chlorine content and oxygen-consuming capacity of the water at the reservoir.

[Results expressed as parts per million.]

Date.	Chlorine.	Oxygen consumed.	Date.	Chlorine.	Oxygen consumed.
1915.					
September 20...	3.5	0.67	October 5.....	3.7	1.33
September 21...	3.5	0.8	October 6.....	3.5	1.43
September 22...	3.5	0.8	October 7.....	3.4	1.27
September 23...	3.5	0.77	October 8.....	4.1	1.29
September 24...	3.5	0.85	October 11-16*	3.9	-----
September 25...	3.5	0.96	October 18.....	3.5	-----
September 27...	3.5	0.71	October 19.....	3.0	-----
September 28...	3.9	0.78	October 26.....	3.6	-----
September 29...	3.8	1.01	October 27.....	3.4	-----
September 30...	4.1	1.23	October 28.....	3.5	-----
October 1.....	3.9	1.30	October 29.....	3.6	-----
October 2.....	3.6	1.26	October 30.....	3.1	-----
October 4.....	3.8	1.01	November 1.....	3.3	-----
			November 2.....	3.3	-----

\* Composite sample.

The constancy of the results in this table show the improvement in the present water supply over that of the old Mariquina system. Thus the chlorine content varied only from 3.5 to 4.1, while that of the old supply (Table I) varied from 2.1 to 4.4; the oxygen-consuming capacity of the former fluctuated between 0.67 and 1.4, that of the latter between 0.65 and 2.2.

Bacteriologically the water shows the fluctuations naturally to be expected from a surface water. After a heavy rain the colony count of the Montalban supply sometimes reaches an enormous figure, although the water as it leaves the reservoir generally has a count below 1,000. Pathogenic organisms in all probability are generally absent, although *B. coli* is occasion-

<sup>5</sup> Standard methods of water analysis (1912), 29.

ally reported. Ciliates, flagellates, and amœbæ are frequently present, but it is doubtful whether these are objectionable, especially as Walker<sup>6</sup> has shown that the amœbæ normally present in water do not cause dysentery, and that the dysenteric amœbæ rapidly die in water.

However, in view of the great fluctuation in bacteria count and the occasional presence of organisms of the *B. coli* group, it is evident that the water should be subjected to some sort of purifying treatment before it is used for domestic supply. The combination of turbidity and high bacterial content would point to filtration as the most logical method of treatment. At the present time large numbers of small fishes, shrimps, and quantities of other foreign substances find their way into the distribution system and give rise to troubles, most of which would be eradicated by filtration.

#### SELF-PURIFICATION AT THE RESERVOIR

Although the Manila city reservoir has only a little over three days' capacity, a surprisingly great degree of bacterial purification seems to be effected during the brief storage period. As the water is often decidedly turbid when it arrives at the reservoir, it is probable that the improvement is due in a great measure to sedimentation. None but preliminary observations on bacterial self-purification have been made, and these only at one season of the year, so that the results are hardly conclusive; however, they show good agreement and probably give a good indication of the magnitude of the purifying action. Samples were taken daily both at the inlet and at the outlet of the reservoir. The average temperature of the water was 26° C. at the inlet and 27° C. at the outlet. The experimental data are given in Table III.

TABLE III.—*Self-purification of water in reservoir.\**

Date.	Inlet.		Outlet.		Reduction.
	Colony count.	Test for <i>B. coli</i> . <sup>b</sup>	Colony count.	Test for <i>B. coli</i> . <sup>b</sup>	
1914.					<i>Per cent.</i>
July 16 .....	2,900	Positive .....	48	Positive .....	98
July 21 .....	2,800	.....do .....	400	.....do .....	86
July 22 .....	425	.....do .....	24	.....do .....	94
July 23 .....	625	.....do .....	48	.....do .....	92
July 30 .....	750	.....do .....	90	.....do .....	88
Average reduction .....					92

\* Examination by O. Schöbl, bacteriologist, Bureau of Science.

<sup>b</sup> In 2 cubic centimeter samples.

\* *This Journal*, Sec. B (1911), 6, 259; (1913), 8, 253.

## CHLORINATION

In spite of the purification effected by storage, the city water as it leaves the reservoir has a rather high bacteria count, and as it is a surface water, there is always a chance of contamination. Therefore chlorination has been resorted to further to purify the water. The method of application is simple. Chloride of lime is mixed with water to form an emulsion, strained to exclude large particles, and poured into the water just as it leaves the reservoir and enters the main service pipe. The addition of disinfectant is regulated according to the flow of water, the latter being determined by means of a Venturi meter. The water has a fairly high velocity and is sufficiently agitated by its own motion to insure thorough mixing within a few minutes.

There are a number of factors militating against the efficiency of the chlorination. The turbidity and high content of organic matter greatly reduce the sterilizing action of the chlorine. Only limited amounts of chloride of lime can be used on account of the disagreeable odor imparted to the water by relatively small additions, probably because of the high temperature (27-29°) of the water and because of the lack of a period of storage between the time the water is chlorinated and the time it enters the service pipes. There is no provision made for destroying any excess chlorine.

Owing to sedimentation in the distribution pipes and to other factors, comparison of the unchlorinated water in the reservoir and the water from the city taps has given confusing results. In the series of observations here enumerated, therefore, it has been found advisable to study the water at two places, the first at the reservoir, the second at a point in the supply pipe where the main distribution system has not been reached and where the velocity of the water has not appreciably diminished. At this second place, located at San Juan bridge, there is a much-used public hydrant in almost direct connection with the main supply pipe at which the water, it is calculated, arrives about forty-five minutes after it leaves the reservoir. As nearly as could be ascertained, by bacteriological tests of the water in different parts of the distribution system, the chloride of lime reached its maximum effect at about this point.

As might be expected, the chemical change in the water caused by chlorination is slight. There is an insignificant increase in turbidity, while alkalinity, hardness, and total solids show no appreciable change. The variation in chlorine and oxygen-con-

suming capacity are shown in Table IV, in which the analyses of water, taken from the Bureau of Science tap, are added for comparison.

At the time these observations were made, chlorination at the rate of approximately 0.5 part of available chlorine per million parts of water was being employed.

TABLE IV.—*Daily variation in chlorine content and oxygen-consuming capacity.*

[Results expressed as parts per million.]

Date.	San Juan.		Tap.	
	Chlorine.	Oxygen consumed.	Chlorine.	Oxygen consumed.
1915.				
September 20.....	4.0		4.0	0.65
September 21.....	4.0	>0.8	4.2	0.7
September 22.....	4.0	0.65	4.0	0.8
September 23.....	4.0	0.77	3.5	0.86
September 24.....	4.0	0.74	4.4	0.88
September 25.....	4.5	0.73	5.0	0.92
September 26.....			4.8	
September 27.....	3.7	0.84	3.4	1.09
September 28.....	3.7	0.85	4.0	0.94
September 29.....	4.0	1.12	4.1	1.47
September 30.....	4.9	1.33	3.7	1.44
October 1.....	4.4	1.23	4.1	2.33
October 2.....	3.8	1.20	3.9	1.40
October 4.....	3.8	0.96	4.1	2.23
October 5.....	6.8	1.17	4.0	1.59
October 6.....	3.9	1.41	3.7	1.62
October 7.....	9.4	0.92	5.5	1.09
October 8.....	4.7	1.20	4.1	1.23
October 9.....	4.4	1.18	3.8	1.49

The results show that the oxygen-consuming capacity<sup>7</sup> increased greatly between the time the water entered the city mains and the time it reached the Bureau of Science, indicating that a large amount of organic matter was taken up by the water in its course through the city distribution system.

In order to study the chloride of lime treatment, daily bacterial examinations were made both at the reservoir and at San Juan bridge. The amounts of disinfectant added were varied, from an addition representing 0.5 part of "available chlorine" in a million parts of water to one representing 0.75 part per million.

<sup>7</sup> Owing to the disturbing influence of small amounts of hypochlorite on the determination of oxygen consumption, the results obtained are not strictly comparable with the data in Table II.

At this latter concentration the odor of the city water was marked, and complaints were so numerous that it was deemed inadvisable further to increase the addition rate.

The effects of different quantities of chlorine are shown in Tables V to IX, inclusive.

TABLE V.—Effect of 0.5 part available chlorine per million parts of water.\*

Date.	Reservoir.		San Juan.		Reduction.
	Colony count.	Test for <i>B. coli</i> group. b	Colony count.	Test for <i>B. coli</i> group. b	
1914.					Per cent.
June 1 .....	110	Positive .....	80	Positive .....	27
June 2 .....	350	Negative .....	80	Negative .....	77
June 3 .....	180	Positive .....	120	Positive .....	33
June 4 .....	38	do .....	26	Negative .....	32
June 5 .....	60	do .....	36	do .....	40
June 6 .....	210	do .....	190	do .....	10
June 7 .....	120	do .....	360	Positive .....	
June 8 .....	48	do .....	36	do .....	25
June 9 .....	34	do .....	26	Negative .....	24
June 10 .....	14	do .....	18	Positive .....	
June 27 .....	10	do .....	8	Negative .....	20
June 28 .....	128	do .....	36	do .....	72
Average reduction less than .....					50

\* Examination by O. Schöbl, bacteriologist, Bureau of Science.

b In 2 cubic centimeter samples. *Bacillus coli* removed six out of eleven times = 55 per cent.

The next series, representing the addition of 0.56 part of chlorine per million, is probably not conclusive because of the uniformly low bacterial content of the water during the time of examination and because of the small number of observations; it is included, however, for the purpose of comparison.

TABLE VI.—Effect of 0.56 part available chlorine per million of water.\*

Date.	Reservoir.		San Juan.		Reduction.
	Colony count.	Test for <i>B. coli</i> group. b	Colony count.	Test for <i>B. coli</i> group. b	
1914.					Per cent.
June 11 .....	70	Positive .....	18	Negative .....	74
June 12 .....	4	do .....	12	do .....	
June 13 .....	48	do .....	18	do .....	63
June 14 .....	46	do .....	16	do .....	65

\* Examination by O. Schöbl, bacteriologist, Bureau of Science.

b In 2 cubic centimeter samples. *Bacillus coli* removed three out of three times.

Another set of observations was made while 0.625 part of chlorine per million parts of water was being added, and as this

rate of addition was employed at two different periods, the two series of tests are recorded independently.

TABLE VII.—Effect of 0.625 part available chlorine per million of water.\*

Date.	Reservoir.		San Juan.		Reduction.
	Colony count.	Test for <i>B. coli</i> group. <sup>b</sup>	Colony count.	Test for <i>B. coli</i> group. <sup>b</sup>	
1914.					Per cent.
June 15.....	18	Positive	4	Negative	78
June 16.....	55	do	12	do	78
June 17.....	95	do	42	do	56
June 18.....	240	do	110	do	54
June 19.....	90	do	14	do	84
June 20 <sup>c</sup> .....	450	do	170	Positive	62
June 21.....	450	do	325	Negative	28
Average reduction in bacteria count.....					63

\* Examination by O. Schöbl, bacteriologist, Bureau of Science.

<sup>b</sup> In 2 cubic centimeter samples. *Bacillus coli* removed six out of seven times=86 per cent.

<sup>c</sup> Typhoon; muddy water.

TABLE VIII.—Effect of 0.625 part available chlorine per million of water.\*

Date.	Reservoir.		San Juan.		Reduction.
	Colony count.	Test for <i>B. coli</i> group. <sup>b</sup>	Colony count.	Test for <i>B. coli</i> group. <sup>b</sup>	
1914.					Per cent.
June 29.....	180	Positive	55	Negative	69
June 30.....	90	do	55	do	39
July 1.....	12	do	4	do	67
July 2.....	12	do	contaminated.		
July 3.....	150	do	18	Negative	88
July 4.....	210	do	10	do	94
July 5.....	750	Negative	46	do	94
July 6.....	600	Positive	85	do	86
July 7.....	1,900	do	1,000	do	47
July 8.....	120	do	95	do	21
July 9.....	130	do	120	Positive	8
Average reduction in bacteria count.....					61

\* Examination by O. Schöbl, bacteriologist, Bureau of Science.

<sup>b</sup> In 2 cubic centimeter samples. *Bacillus coli* removed eight out of nine times=89 per cent.

The greatest addition of chloride of lime, representing 0.75 part of free chlorine per million of water, was employed for only a short time, because of the complaints against the disagreeable odor of the water.<sup>8</sup>

<sup>8</sup> Recent experiments would indicate that the disagreeable odor was in reality due to irregularities in dosing the water at certain times of the day. There is good reason to believe, however, that during the hours the samples for the series of experiments here enumerated were taken chlorination proceeded with regularity and at the rates recorded.

TABLE IX.—Effect of 0.75 part of free chlorine per million of water.\*

Date.	Reservoir.		San Juan.		Reduction.
	Colony count.	Test for <i>B. coli</i> group. <sup>b</sup>	Colony count.	Test for <i>B. coli</i> group. <sup>b</sup>	
1914.					Per cent.
June 22.....	275	Positive .....	130	Negative .....	35
June 23.....	450	do .....	70	do .....	84
June 24.....	120	do .....	48	Positive .....	60
June 25.....	190	do .....	38	Negative .....	80
June 26.....	150	Negative .....	44	do .....	71
Average reduction in bacteria count .....					65

\* Examination by O. Schöbl, bacteriologist, Bureau of Science.

<sup>b</sup> In 2 cubic centimeter samples. *Bacillus coli* remained in one instance.

It will be noted that in no case has the sterilization efficiency reached a figure comparable with those generally reported. According to a committee report to the American Public Health Association<sup>9</sup> the bacterial reduction which may be reasonably expected of typical installations in American cities is about 98 per cent, with which the 50 to 70 per cent reductions here obtained compare rather poorly. However, since the Manila water comes from a watershed well guarded against trespass, pathogenic organisms are probably absent or at any rate very few in number; and since the pathogenes succumb more readily than other forms to the attack of chloride of lime, it is reasonable to suppose that the water is safer, so far as potability is concerned, than would appear from the actual reduction in bacteria count. It is interesting to note the greatly increased efficiency of 0.625 part of available chlorine per million as compared with 0.5 part and the relatively slight increase in efficiency of 0.75 part over 0.625.

The results of these tests show that hypochlorite treatment is not adapted to a turbid water high in organic matter. The high temperature of the Manila water is an added complicating factor which probably accounts in a large measure for the disagreeable odor chlorination imparts to the water.

The low efficiency of the chlorination treatment finds a ready explanation in the high chlorine-consuming power of the Montalban water. The results of the chlorination tests indicate both that a large amount is taken up immediately, which accounts for the low efficiency of small additions of chloride of lime, and that the reaction proceeds more slowly with time, though a definite end point is not reached for many hours, so

<sup>9</sup> *Am. Journ. Pub. Health* (1915), 5, 918.

that even the higher concentrations of chlorine failed to operate successfully. It is known that waters have the power of chemically combining with free chlorine, and as pointed out by Haiiri,<sup>10</sup> this power varies widely for different waters. This chlorine-consuming capacity is not equal or necessarily proportional to the oxygen-consuming capacity, although a high organic content is generally associated with a high chlorine-consuming capacity. A few rough experiments on the unchlorinated water from the city reservoir showed that the chlorine consumption in one hour varied from 0.5 to 1.0 part per million of chlorine consumption in samples taken on different days.

The chlorine consumption was determined by digesting reservoir water in the dark with a measured amount of clear, filtered chloride of lime solution of known strength, and determining the available chlorine from time to time by adding potassium iodide and phosphoric acid,<sup>11</sup> and titrating the liberated iodine with 0.02 N sodium thiosulphate solution, using starch indicator.

Adding a quantity of chloride of lime corresponding to 1 milligram of available chlorine per liter of water, approximately 60 per cent was generally used up in one hour. A typical series of determinations follows:

TABLE X.—*Decomposition of chloride of lime in water.\**

Digestion.	Chloride of lime.	
	Left.	Consumed.
Hrs. min.		
0 3	0.8	0.2
0 35	0.45	0.55
1 45	0.35	0.65
3 45	0.20	0.80
20 0	0.14	0.86

\* One milligram available chlorine added per liter of water.

The results obtained show how rapidly the chlorine loses its effect. It is possible that the chlorine has such highly selective action that dangerous organisms are generally eliminated; however, the bacteriological data (Tables V to IX) indicate that the chlorine loses its effect before the bacteria count is sufficiently reduced to render the water absolutely safe.

<sup>10</sup> *Zeitschr. f. Hyg.* (1913), 75, 46.

<sup>11</sup> Winkler, *Zeitschr. f. angew. Chem.* (1915), 28, 1.

## RELATION BETWEEN CHEMICAL AND BACTERIOLOGICAL DATA

I have tried without much success to correlate the chemical analyses with the bacteriological data at hand. It is noteworthy that the water was almost constant in composition during the period of observation, in spite of the enormous fluctuations (from 120 to 10,000) in the daily colony counts during that time.

The chlorine content was almost constant, its slight variation showing no traceable connection with the fluctuation in bacterial content. There was no apparent relation between chlorine content and oxygen consumed. It is, therefore, evident that except for sudden and great contamination the chlorine content of the city water supply is of little significance.

Barnard<sup>12</sup> and others have repeatedly pointed out that a high nitrogen content is not always an indication of contamination and have shown the futility of isolated nitrogen determinations. This is confirmed by the results obtained in this laboratory and by a critical study of the work on the city water supply previously quoted,<sup>13</sup> in which there is no traceable connection between the bacteria counts and nitrogen determinations, though both showed great variations.

The best indication of the purity of the water was probably furnished by the oxygen-consuming capacity, which showed a number of maxima and minima corresponding fairly well with bacteriological data, but here, too, the agreement was not very good.

In short, little more than the rather trite statement that in a series of determinations made at short intervals a high bacteria count generally appears to be associated with a high organic content seems to be justified. The truth of this is further indicated by the following analysis of the results of the studies on Manila water:

TABLE XI.—*Relation between bacterial content and oxygen-consuming capacity.*

Series No.	Year.	Source.	Oxygen consumed.	Average colony count per cubic centimeter.	Determinations.
1	1903-4	Tap.....	>1.5	360	5
	1903-4	do.....	<1.5	195	18
2	1915	Reservoir.....	>1.0	4,300	10
	1915	do.....	<1.0	3,400	7

<sup>12</sup> *Eng. Rec.* (1913), 68, 297.

<sup>13</sup> Bliss, *Pub. P. I. Bur. Govt. Lab.* (1905), No. 20, 10.

## SUMMARY AND CONCLUSIONS

The present water supply of Manila, although insufficient in amount during dry seasons of long duration, is a vast improvement over the old supply.

Chemically the water is satisfactory for domestic use, but its bacterial content makes artificial purification necessary. Preliminary experiments indicate that the self-purification of the water in the reservoir was about 90 per cent, although the average storage period was only a little over three days.

Chlorination effected a bacterial reduction of less than 70 per cent. Turbidity, temperature, and especially chlorine-consuming capacity are the factors probably accounting for the low efficiency of the treatment.

The oxygen consumption seems to be the chemical factor which gives the best indication of fluctuations in quality of the water and which shows the greatest similarity with bacteriological data.

Of the procedures discussed, it appears obvious that a daily determination of the oxygen-consuming capacity, supplemented by a bacteriological colony count and a test for the presence or absence of *B. coli*, furnishes the most reliable data concerning the quality of the water. In addition, the frequent determination of chlorine-consuming capacity is of great help in fixing the amount of chloride of lime that will be most effective.

## PHILIPPINE BEESWAX<sup>1</sup>

By HARVEY C. BRILL and FRANCISCO AGCAOILI

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Manila, P. I.)

The determination of the purity of beeswax is a somewhat difficult matter, especially so when the adulteration is slight or ingenuity has been practiced in the preparation of the adulterated product.

Seiichi Neno<sup>2</sup> has given figures for the beeswax of Korea and states that these are not different from the constants of the beeswax of Japan and India, but are different from the constants for the European and American products.

The beeswax of Korea is produced by *Apis indica*; that of India by *A. indica*, *A. florea*, and *A. dorsata*; that of Europe and America by *A. mellifica*; that of the Philippine Islands by *A. zonata*, *A. dorsata*, and *A. indica*. According to the figures given by the Bureau of Customs of the Philippine Islands<sup>3</sup> 42,602 kilograms of beeswax were exported in 1913 and 44,148 kilograms in 1914.

In view of the difference in the properties of the Japanese and Korean waxes from the European and American and the likelihood of the local waxes being different and in order that standards might be established for the determination of the purity of any samples submitted for examination and thus honesty in the preparation of the commercial product be encouraged, the Bureau of Science has determined the constants of a number of samples of local beeswax.

Samples were purified by boiling in water, then separating from the impurities and drying at 100° C.

For the purpose of comparison some results found by Shibasaki<sup>4</sup> for Japanese beeswax and by Neno<sup>5</sup> for Korean beeswax are included.

<sup>1</sup> Received for publication January 11, 1916.

<sup>2</sup> *Analyst* (1915), 40, 343.

<sup>3</sup> Bur. Customs, Foreign Commerce of the Philippine Islands, Manila (1915).

<sup>4</sup> *Analyst* (1915), 40, 343.

<sup>5</sup> *Ibid.*

TABLE I.—Constants of Philippine beeswaxes.

Sam- ple No.	Origin.	Color or qual- ity.	Specific gravity at 15.5°C.	Melting point.	Saponi- fication value.	Acid value.	Ester value.	Ratio number.	Iodine value (Hanus).	Unsa- ponifi- able.	Clouding point.
					°C.					Per cent.	°C.
1	Catanduanes .....	Yellow .....	0.9739	62.0	100.5	7.5	93.0	12.4	10.8	56.8	59.5
2	Caluyugan barrio, Santa Maria, Laguna .....	White <sup>a</sup> .....	0.9654	64.5	107.0	6.9	100.1	14.5	10.4	58.6	59.5
3	Napsan, municipality of Princessa, Palawan Province .....	Refined <sup>a,b</sup> .....	0.9226	63.5	106.8	7.7	99.1	12.9	9.2	60.4	60.0
4	Babuyan .....	Crude <sup>c</sup> .....	0.9554	63.0	104.8	7.9	96.9	12.3	8.4	54.7	59.0
5	Marcosatubig, Zamboanga, Mindanao .....	Refined <sup>a</sup> .....	0.9309	62.0	101.4	6.8	93.6	13.8	9.2	55.4	60.0
6	Basao, Gattaran, Cagayan .....	Crude <sup>d</sup> .....	0.9641	64.0	103.9	6.3	97.6	15.5	8.8	55.6	59.0
7	Davao, Mindanao .....	do .....	0.9654	63.5	103.4	7.6	95.8	12.6	9.6	55.6	59.5
8	Do .....	Refined <sup>a</sup> .....	0.9589	63.0	98.2	6.9	91.3	13.2	8.5	51.6	60.0
9	Caligayan, Isabella .....	Crude .....	0.9891	63.0	96.3	6.3	90.0	14.3	8.2	57.0	60.0
10	Panakan, Davao, Mindanao .....	do .....	0.9481	63.5	99.8	6.3	93.5	14.8	7.4	57.8	59.5
11	Bongon, Davao, Mindanao .....	do .....	0.9918	64.0	99.4	6.2	93.2	15.0	9.6	53.0	59.0
12	Pili barrio, Surigao, (Mindanao) .....	do .....	0.9565	63.0	100.5	6.4	94.1	14.7	8.5	52.7	60.0
13	Ilog barrio, Mindoro .....	do .....	0.9601	62.5	99.8	6.0	93.8	15.6	8.6	55.3	60.0
	Maximum .....		0.9918	64.5	107.0	7.9	100.1	15.6	10.8	58.6	60.0
	Minimum .....		0.9309	62.0	96.3	6.0	90.0	12.4	7.4	51.6	59.0
	Average .....		0.9601	63.2	101.7	6.8	94.8	13.9	9.0	55.7	59.6

<sup>a</sup> Refined by boiling in water.<sup>b</sup> First class.<sup>c</sup> Not refined.<sup>d</sup> Third class.

TABLE II.—Constants for Japanese and Korean beeswaxes.

	Japanese.			Korean.		
	Maximum.	Minimum.	Average.	Maximum.	Minimum.	Average.
Specific gravity at 100 °C.	0.8207	0.8135	0.8160	0.8358	0.8090	0.8229
Melting point .....°C.	66.5	64.9	65.9	65.0	65.0	65.6
Saponification value.....	103.34	86.35	89.85	87.72	79.24	84.56
Acid value.....	8.19	5.61	6.40	7.70	4.46	5.85
Ester value.....	95.14	80.45	83.44	87.98	74.23	78.71
Ratio number.....				17.63	10.23	13.45
Iodine value (Wijs).....	14.14	10.18	12.27	12.93	10.04	11.41

A study of the average values of the constants of Tables I and II brings out the fact that they differ somewhat, namely, the specific gravities are not comparable since they have been determined at different temperatures; the melting points run 63.2, 65.9, and 65.6, respectively, for the Philippine, Japanese, and Korean products; the saponification values are 101.7, 89.85, and 84.56 in the above order; the acid values 6.8, 6.4, and 5.85 in the same order; the ester values 94.8, 83.44, and 78.71 in the same order; and the ratio numbers 13.9 and 13.45, respectively, for the Philippine and Japanese waxes. The unsaponifiable portion for the Philippine product averages 55.7 per cent, which is somewhat higher than 52.38 per cent, the value given by Allen and Thomson<sup>6</sup> for beeswax. The clouding point has been included. This value was determined according to the directions of Salamon and Seaber.<sup>7</sup> The authors saponify 1 gram of wax for one hour with 20 cubic centimeters of N/4 alcoholic potash. The flame is then removed, a thermometer inserted, and the liquid stirred continuously until the solution becomes cloudy. The end point is sharp and constant. In the case of pure waxes the cloudiness is followed by the immediate appearance of a flocculent precipitate; with adulterated samples the clouding is gradual and flocculation does not occur until a lower temperature is reached. Under the above conditions they assert that genuine beeswax of the European type (acid value 17 to 20, ester value 68 to 78, a definition including many African samples) clouds at  $60 \pm 0.5^\circ \text{C.}$ , and that East Indian (including Chinese) beeswaxes cloud at  $56.5 \pm 0.5^\circ \text{C.}$  As little as 5 per cent of paraffin wax (melting point  $50^\circ$  to  $60^\circ \text{C.}$ ) raises the clouding point of European waxes to  $64^\circ$  and East Indian

<sup>6</sup> *Chem. News* (1881), 43, 267.<sup>7</sup> *Journ. Soc. Chem. Ind.* (1915), 34, 461.

to 62° C.; 10 per cent raises it to 74° and 70° C., respectively. By ingenious compounding, beeswax can be adulterated with paraffin and with tallow, resin, or Japanese wax without a deviation in the saponification value and with very slight change in the melting point. In such cases the clouding point would be useful in the detection of the adulteration.

#### SUMMARY

The constants for Philippine beeswax are given in Table I. Comparison of these with the constants of the Japanese and Korean is made.

The clouding point of the local beeswax compared with that for European and East Indian waxes is added.

# THE POZZUOLANIC PROPERTIES OF MEYCAUAYAN VOLCANIC TUFF<sup>1</sup>

By ALBERT E. W. KING

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## ONE TEXT FIGURE

During June, 1914, the Bureau of Science received for compression test twelve 6-inch tuff (adobe stone) cubes taken from the Tayawanak quarry, Cavite Province, Luzon. Similar material was to be used in the construction of bridge abutments. The specimens were exposed in air and tested for compressive strength. Table I shows the results obtained.

TABLE I.—Compressive strength of 6-inch Tayawanak tuff cubes.

Age.	Total strength.				Strength per square centimeter.		Strength per square inch.	
	First crack.	Ultimate.	First crack.	Ultimate.	First crack.	Ultimate.	First crack.	Ultimate.
Days.	Kilos.	Kilos.	Lbs.	Lbs.	Kilos.	Kilos.	Lbs.	Lbs.
35	1,315	1,394	29,000	30,750	56.66	60.04	806	854
35	545	1,042	12,000	22,950	23.41	44.85	333	638
35	516	1,262	11,350	27,800	22.14	54.34	315	773
35	523	1,098	11,500	24,200	22.42	47.31	319	673
35	882	1,098	19,400	24,200	37.82	47.31	538	673
35	302	925	6,650	20,350	13.00	39.79	185	566
63	999	1,476	23,000	32,500	44.85	63.48	638	903
63	1,184	1,248	26,100	27,500	50.97	53.71	725	764
63	908	1,161	20,000	25,550	39.09	49.77	556	708
63	1,348	1,348	29,700	29,700	28.00	58.00	825	825
63	1,549	1,549	34,100	34,100	66.65	66.65	948	948
63	550	1,057	12,100	23,300	23.60	45.48	336	647

The material is very soft, porous, and fine-grained and as the results show is not suitable for construction subjected to high unit stresses. Cox<sup>2</sup> describes the occurrence and properties of tuffs in general:

..... volcanic sediments and pyroclastic tuffs occur quite widely distributed in the Philippines. They are especially abundant in west central Luzon, extending almost unbrokenly from near Lingayen Gulf to the sea-coast of Batangas, practically blanketing or covering nearly all of the massive rocks of this region. Mr. Ickis found volcanic tuff in the Agusan Pulangi region, interior from Cagayan Misamis.

In the absence of a better stone, in certain places this has been used extensively for building purposes. In Bulacan and along the Pasig River,

<sup>1</sup> Received for publication December 21, 1915.

<sup>2</sup> *This Journal*, Sec. A (1908), 3, 393.

especially near Guadalupe, this stone is unusually abundant. Large quantities of it have been quarried and used in the construction of many churches and other buildings and in the walls and fortresses of Manila. It is very workable. Before it is distributed it is so soft that it can be quarried with an axe, but it hardens rapidly on exposure.

Philippine tuffs vary considerably in texture, color, density, and chemical composition. Some are fine-grained and soft like those quarried at Santa Mesa, Rizal, and at Tayawanak, Cavite; others are coarse-grained and hard like those taken out in the vicinity of Meycauayan, Bulacan. The harder varieties are preferred for construction, though much of the softer material is used locally because it is cheaper. Cox<sup>3</sup> reports a microscopic examination of the tuff found in the vicinity of Manila and shows it to be composed of (1) feldspar, (2) magnetite, (3) hornblende, (4) quartz, (5) and a cementing material, largely composed of oxide of iron.

It was thought that the spalls and débris remaining after the compression test on the Tayawanak tuff might possess pozzuolanic properties if finely ground and mixed with hydrated lime. The problem is not a new one, but there seem to be no published results on the properties of Philippine tuffs when mixed with slaked lime. Such an investigation should be of considerable local industrial value. Trass or pozzuolan cements were used by the ancients and are still used to a considerable extent in Europe. Vitruvius and Pliny both make mention of their utility. Of late, considerable activity has been shown in various circles regarding the efficacy of tuffs mixed with Portland cement when the latter is to be used in sea water.<sup>4</sup> Although the tuff mixtures studied in this laboratory do not harden to the same degree as does Portland cement, nevertheless they could be used very advantageously under certain conditions as a cheap and efficient building material.

<sup>3</sup> Loc. cit.

<sup>4</sup> Duryee, Puzzolan-Portland cement; a suggestion for an improved hydraulic cement. *Eng. News* (1910), 64, 596.

Gebrauch von Trass bei Eisenbeton. *Tonind.-Zeitg.* (1913), 37, 1857.

Poulsen, A., Diatomeerde als Puzzolane. *Tonind.-Zeitg.* (1913), 37, 1132. (Mixing of Portland cement with ground diatomaceous earth.)

Duryee, E., Further investigations of Puzzolan-Portland cements. *Eng. News* (1912), 68, 297.

Martin, Hr., Über den Wert von Trass Zuschlägen zum Zement und Kalkmörtel (1914), 13, 286-8, 298-306.

Lippincott, J. B., Tufa cement as manufactured and used on the Los Angeles aqueduct. *Chem. Ab.* (1911), 5, 1672; (1913), 7, 236.

Jacobs, E., Use of trass in reinforced concrete. *Ingenieur*, 27, 134-8. See *Chem. Ab.* (1913), 7, 237.

# PRELIMINARY WORK

For the purpose of ascertaining whether or not the Tayawanak tuff possessed any hydraulic properties, the fragments remaining after the compression test were dried in the sun, reduced in a crusher, and ground in a ball mill until 100 per cent passed through a sieve having an average of 22,500 meshes per square inch. Dry slaked lime, containing 96.98 per cent calcium hydroxide, and the pulverized tuff were mixed in equal parts by weight. The lime had the same fineness as the tuff. The resulting mixture, after being tempered with water in the usual way and allowed to harden, was tested for compressive and tensile strengths and setting time. In the test pieces 27 per cent of water was used. After two days in moist air the specimens were stored in water until broken.

The approximate setting time was determined by the Gilmore needle.

In Table II are tabulated the results obtained.

TABLE II.—*Tensile strengths of briquettes and compressive strengths of 2-inch cubes made from tuff fragments.*<sup>a</sup>

## TENSILE STRENGTH OF BRIQUETTES.

	Kilo-grams per square centi-meters.	Pounds per square inch.
7 days neat (2 days in moist air, 5 days in water) .....	11.60	165
90 days neat (2 days in moist air, 88 days in water) .....	17.53	250
180 days neat (2 days in moist air, 178 days in water) .....	18.71	266
7 days mortar (2 days in moist air) <sup>b</sup> .....	9.98	142
90 days mortar (2 days in moist air) <sup>b</sup> .....	21.45	305
180 days mortar (2 days in moist air) <sup>b</sup> .....	26.72	380

## COMPRESSIVE STRENGTH OF 2-INCH CUBES.

	Kilo-grams per square centi-meter.	Pounds per square inch.
7 days neat (2 days in moist air) .....	71.52	1017
28 days neat (2 days in moist air) .....	78.69	1119
90 days neat (2 days in moist) .....	218.28	3104
180 days neat (2 days in moist air) .....	268.42	3817

<sup>a</sup> Initial setting time, 23 hours.

<sup>b</sup> Briquettes were made from one part by weight of the tuff-lime mixture and three parts by weight of standard Ottawa sand.

When mixed with lime, the tuff exhibits very marked hydraulic properties, developing considerably higher compressive strength per unit area than the original tuff blocks as taken out of the quarry. The tensile strength of the mortar at the 90- and 180-day periods is greater than that of the corresponding neat briquettes and equals the strength of the average Portland cement-mortar briquettes tested in the Bureau of Science. The results show that the tuff possesses well-defined pozzuolanic properties. The quarry where this tuff was obtained unfortunately has little economic importance at present because it is situated in the interior of Cavite Province at a considerable distance from both rail and water transportation. It was, therefore, decided to use a different tuff in making the more extensive tests. The tuff obtained near Meycauayan, Bulacan Province, was finally chosen because of the favorable location of the quarry and the superior quality of the material.

On April 6, 1915, I made a trip to the quarry at the barrio of Ligtong on Ligtong River, about twenty minutes' walk from the Meycauayan railroad station. The quarry, known as "Tibagan," is owned by Francisco Carreon. The Tibagan is one of the oldest tuff quarries near Manila, having been worked during the early Spanish period. It furnishes the hardest and most durable tuff found on the Manila market. It is of interest to note that the quality of the tuff in this one quarry is variable; some pits produce a much softer stone than adjacent ones and are for that reason preferred by the workmen, since quarrying is easier. Large quantities of *débris* resulting from the dressing and quarrying of the tuff are strewn about; these served as the source of the sample secured for this investigation.

#### EXAMINATION OF THE MEYCAUAYAN TUFF

A megascopic examination of the Meycauayan tuff shows it to be constituted of comparatively large, irregular fragments of igneous material embedded in a fine-grained matrix. It may be designated as a water-laid agglomerate. Most of the coarser components are volcanic ejecta. These cemented ejecta consist of sharp fragments of basalt, coarse pieces of pumice, volcanic glass, and scoria. The tuff is gray, with a bluish green cast. It is fairly resistant, but is easily scratched with the sharp point of a pocket knife.

An analysis of the tuff is given in Table III.

TABLE III.—*Analysis of Meycauayan tuff.*<sup>a</sup>

Constituent.	Per cent.
Insoluble silica (SiO <sub>2</sub> )	42.81
Soluble silica (SiO <sub>2</sub> )	12.22
Aluminium oxide (Al <sub>2</sub> O <sub>3</sub> )	7.12
Ferric oxide (Fe <sub>2</sub> O <sub>3</sub> )	16.56
Calcium oxide (CaO)	5.53
Magnesia (MgO)	2.24
Sodium and potassium oxides (K <sub>2</sub> O + Na <sub>2</sub> O)	5.34
Water at 110°C.	3.09
Loss on ignition <sup>b</sup>	4.34

<sup>a</sup> Analysis by Rafael H. Aguilar, chemist, Bureau of Science.

<sup>b</sup> Mostly water above 110° C.

The percentage of soluble silica is low. No published results of soluble-silica determinations on Philippine tuffs are at hand for comparison, and it is impossible to state whether the quantity found here is characteristic of Philippine tuffs in general or is a peculiarity of the Meycauayan tuff. Kiushi volcanic ash, produced at Karatsu, Sagaken, Japan, and analyzed at the Industrial Experimental Station at Osaka, contains 19.99 per cent of soluble silica. When compared with the results obtained by E. Schwarz in his investigation of some European tuffs possessing well-defined hydraulic properties, the result is also low.<sup>5</sup>

About 84 per cent of the tuff used for this determination passed through the 200-mesh sieve. The error introduced in the analysis with this fineness due to the solvent action of the alkali upon the quartz is very slight and ordinarily can be neglected. Lunge and Millberg<sup>6</sup> state that it reaches from 0.1 to 0.2 per cent of the total amount of silica. As a result the percentage of amorphous silica obtained will be in excess of that actually present. If anything, therefore, the results shown are probably too high.

<sup>5</sup> The method of determining the soluble silica in Table III is based upon the procedure recommended by W. Hillebrand in The analysis of silicate and carbonate rocks [*Bull. U. S. Geol. Surv.* (1906), 305, 165]. According to G. Lunge and Milberg [*Zeitschr. f. angew. Chem.* (1897), 393, 425], quartz is not nearly so insoluble in solutions of the caustic alkalies as has been supposed; if given a sufficient degree of subdivision, it can be brought wholly into solution. It is impossible to secure correct separation of quartz and opaline silica by the use of either caustic or carbonated alkalies. Digestion on the water bath for fifteen minutes with 5 per cent solution of sodium carbonate is the only way to secure exact separation of unignited precipitated silica from quartz, and then only when the finest flour has been removed by levigation.

<sup>6</sup> Loc. cit.

One gram of the finely ground tuff was digested in a Jena beaker with dilute hydrochloric acid for eight hours. The insoluble residue was separated from the liquid by filtration. The residue with the filter paper was transferred to a platinum dish and digested for fifteen minutes with a 5 per cent solution of sodium carbonate on the water bath. The soluble silica was determined in the filtrate.

The method employed by Schwarz,<sup>7</sup> is practically the same, except that he digests for a longer time with sodium carbonate. Some of the results obtained by him are shown in Table IV.

TABLE IV.—Soluble silica in various materials, as recorded by Schwarz.

	Per cent.
Tuff from Rottenheim	17.75
Nettetal tuff	35.75
Brohl tuff	28.95
Vulkan trass	24.74
Mountain trass	27.89
Tuff from the Imperial Construction Bureau of Celle	35.80
Tuff from Hungary	34.80

#### THEORIES OF HYDRAULICITY

Soluble silica is considered by several authorities as being the cause of the hydraulic properties of tuffs and other pozzuolanic materials. Kasai<sup>8</sup> shows that the strength of Portland cement-pozzuolan mortars is directly proportional to the percentage of soluble silicic acid contained in the added pozzuolan. Johnson<sup>9</sup> says:

While the exact chemical reactions have not yet been determined for slag cements, it seems certain that the hardening of slag cements consists of a gradual action of an active form of silica on the free lime, as in the case of pozzuolanas or trass.

Dammer<sup>10</sup> states:

The natural pozzuolanas have the property in common of containing appreciable amounts of silicic acid which react with the added lime and by substitution form the necessary compounds for the induration of the mortar.

On the other hand, there are investigators who maintain that the hydraulic properties of pozzuolanas, tuffs, and trasses are

<sup>7</sup> *Tonind.-Zeitg.* (1912), 36, 1122.

<sup>8</sup> Portlandement with Puzzolanzusatz. *Tonind.-Zeitg.*, G. m. b. H., Berlin (1911). Abstracted in *Tonind.-Zeitg.* (1911), 35, 1644.

<sup>9</sup> The Materials of Construction. John Wiley & Sons, New York (1912), 191.

<sup>10</sup> Chemische Technologie der Neuzeit. Stuttgart, Verlag von Ferdinand Enke (1910), 741.

due to the presence of water of hydration, which, as it were, predisposes the material to chemical activity when mixed with hydrated lime and tempered with water. The Meycauayan tuff contains only 4.34 per cent of water of hydration, which is considered low for this class of material. The German Society for the Testing of Technical Material, in October, 1909, adopted new norms for the testing of tuffs and specified a minimum content of 7 per cent of water of hydration. Water undoubtedly has had a great deal to do in determining the chemical and physical properties of tuffs, but just to what extent is a question which has as yet not been completely solved. Tetmajer<sup>11</sup> has shown that blast-furnace slags, analogous in every way to natural slag such as is investigated in this paper, when allowed to cool in the ordinary way into a solid mass and then crushed to powder, with the addition of lime, exhibit no hydraulic properties to speak of, whereas by suddenly cooling the melted vitreous slag in water a product is obtained that possesses very pronounced hydraulic properties when mixed with lime. In fact, some tuffs that have been deprived of their water of hydration by heating to 700° C. no longer show hydraulic properties. This led Tetmajer to make the statement that the efficacy of tuffs and trasses as cementing material could be judged according to the loss on ignition.

F. Tannhaeuser<sup>12</sup> is of altogether a different mind concerning the cause of the hydraulicity of trasses. He maintains that the pozzuolanic properties of trass from the Brohl and Nette Valleys depend upon the content of sodalite minerals which are found in the groundmass. Tannhaeuser has shown that the alkalies of the sodalite minerals are replaced by the calcium of the hydrated lime with the formation of difficultly soluble silicates and that a precipitation of chemically active silicic acid does not occur at this time. Furthermore he concludes from his investigation that the water content has nothing to do with the hydraulic activity of the tuff.

Pozzuolanas or tuffs possessing marked hydraulic properties vary widely in their chemical and mineralogical compositions. They are not fixed chemical compounds having a constant com-

<sup>11</sup> Vol. 7, 95, cited by Johnston in the *Materials of Construction*. John Wiley & Sons, New York (1912), 95.

<sup>12</sup> Ein Beitrag zur Petrographie des Trasses und zur Erklärung seines hydraulischen Wirkungsweise. Bautechnische Gesteinuntersuchung, *Mitt. a. d. Min.-Geol. Inst. d. k. Tech. Hochschule* (1911), 2, 34-44. Abstracted in *Tonind.-Zeitg.* (1912), 36, 739.

position, but rather mechanical mixtures of several compounds. Hydraulicity does not depend entirely upon the ultimate chemical composition, upon the presence of opaline silica, nor upon the presence of water of hydration. In the light of present knowledge it seems as though hydraulicity depends upon a number of factors, which apparently vary with the material. The mineralogical composition of the tuff is an important factor in this connection and has been overlooked by several investigators. To be able conclusively to prove the cause of the induration under water of pozzuolanas or tuffs when mixed with lime involves a study of the minerals present in the original material before mixing with lime and a study of the compounds and minerals formed after mixing and the addition of water. With the aid of the mineralogical microscope it would be possible to identify such compounds as are formed.

#### PREPARATION OF THE RAW MATERIALS

##### TUFF

The entire sample of tuff, amounting to about 272 kilograms, was first reduced in a jaw crusher to the size of a hazelnut and then fed into a gyratory grinder. The product from the gyratory grinder was comminuted to a fineness of approximately 80 per cent through the 200-mesh sieve. No difficulty was encountered during the reduction process. Although considered locally as a hard tuff, the material, judged from a technological standpoint, is very soft. During the preliminary reduction in the jaw crusher, what especially attracted my attention was the apparent ease with which the tuff was disintegrated; there was an entire absence of flying fragments, sharp snapping, and straining of machine parts, such as are characteristic when crushing even a soft limestone. The softness of the material would be of considerable advantage in case the tuff were used commercially in the manufacture of a pozzuolan cement; grinding costs could be maintained at a minimum. The tuff was not dried, but was ground just as taken out of the quarry. Analysis showed 3.09 per cent moisture. The sample was collected during the dry season, which accounts for the comparative absence of water.

##### LIME

The lime used was made from Montalban limestone in the Bureau of Science experimental kiln. This stone is hard, fine grained, and has grayish to bluish and yellowish tinges. An analysis made by F. B. Beyer, formerly chemist of the Bureau of Science, gave the following composition:

TABLE V.—*Composition of limestone from Montalban.*

	Per cent.
Moisture	0.25
Silica (SiO <sub>2</sub> )	0.94
Ferric and aluminium oxides (Fe <sub>2</sub> O <sub>3</sub> plus Al <sub>2</sub> O <sub>3</sub> )	1.14
Calcium oxide (CaO)	54.61
Magnesia (MgO)	0.22
Loss on ignition	42.79

The calcined product is white, with a slight yellowish tinge. It slakes very rapidly and violently, evolving considerable heat. When sufficient water is added to form a paste, the resulting mass is very plastic and shows the characteristic properties of a fat lime. For this investigation the quick lime was dry slaked by sprinkling with just sufficient water to produce a fluffy, dry, impalpable powder. The slaked powder was separated from lumps of quicklime and the underburned material by sieving through a 100-mesh sieve.<sup>13</sup> The fine lime powder was very white and showed the following composition:

 TABLE VI.—*Composition of fine lime powder from lime made from Montalban limestone.\**

	Per cent.
Silica (SiO <sub>2</sub> )	0.58
Aluminium oxide (Al <sub>2</sub> O <sub>3</sub> )	0.11
Ferric oxide (Fe <sub>2</sub> O <sub>3</sub> )	0.41
Calcium oxide (CaO)	74.04
Moisture	23.56
Carbon dioxide (CO <sub>2</sub> )	0.30
Magnesia (MgO)	0.93
Sodium and potassium oxides (K <sub>2</sub> O plus Na <sub>2</sub> O)	0.30

\* Analysis by R. H. Aguilar, chemist, Bureau of Science.

#### MIXTURES OF TUFF AND HYDRATED LIME

Tests were carried out on three different mixtures containing 90, 75, and 50 per cent of tuff mixed with 10, 25, and 50 per cent of hydrated lime, respectively. The tuff and lime were weighed separately and mixed, for fifteen minutes, in a ball mill. The mixes were designated as A, B, and C, respectively. They had the appearance of ordinary Portland cement, except the color was somewhat lighter; this difference in color was more noticeable when the tuff mixtures were made up into

<sup>13</sup> The resulting powder when placed in a metal drum preparatory to incorporation with the tuff exhibited a property that very closely approached the flow of a liquid when the container was moved. This phenomenon is due to the film of air that surrounds the minute particles and keeps them in suspension, thus reducing friction to a minimum.

specimens. Mix C having the largest amount of lime had the lightest color; it resembled in appearance white Portland cement. The following tests were made: (1) Percentage of water necessary for normal consistency; (2) fineness; (3) specific gravity; (4) setting time; (5) tensile strength, neat, in air; (6) tensile strength, neat, in water; (7) tensile strength, mortar, in air; (8) tensile strength, mortar, in water; (9) compressive strength, neat, in air; (10) compressive strength, neat, in water; (11) compressive strength, mortar, in air; (12) compressive strength, mortar, in water. All mortars were made with one part by weight of the tuff-lime mixture and three parts by weight of standard Ottawa sand.

#### RESULTS OF TESTS

The results obtained are shown in Table VII.

Fig. 1 shows curves obtained by plotting the tensile and compressive strengths in pounds per square inch against time in days. There is a very marked difference in curve slope between air specimens and those kept in water. The strength of those specimens stored in air is practically negligible, whereas the strength developed by some of the test pieces kept in water is considerable. The compressive neat strengths in water of mix C are remarkable in that the curve is practically a straight line and at ninety days still does not show any tendency to parallelism to the X-axis as do the rest. The increment in strength per unit of time during ninety days is constant—about 300 pounds. All other specimens show a falling off in the increment of strength after the 60-day period. When the neat specimens of mixture C stored in water were tested at the 90-day period, failure was accompanied by a sharp report; the spalls had a stonelike ring. The ultimate strength per square inch is 2,202 pounds.

Mix A gave good results, also, although the unit strength did not reach the high figure shown by mix B.

All test specimens, with the exception of those made out of mix C, were allowed to remain in moist air for two days just as made without removing the molds. Mix C was kept in moist air with molds for five days on account of the softness of the specimens. I tried removing some of the test pieces at the end of the second day, as in the case of mixes A and B, but found them so frail that removal without injury was impossible. Two series of tests were conducted upon the various mixtures. One half was stored in air, and the other half was immersed in water. It is common practice in making tests of these kinds to keep the specimens in moist air for a short period,

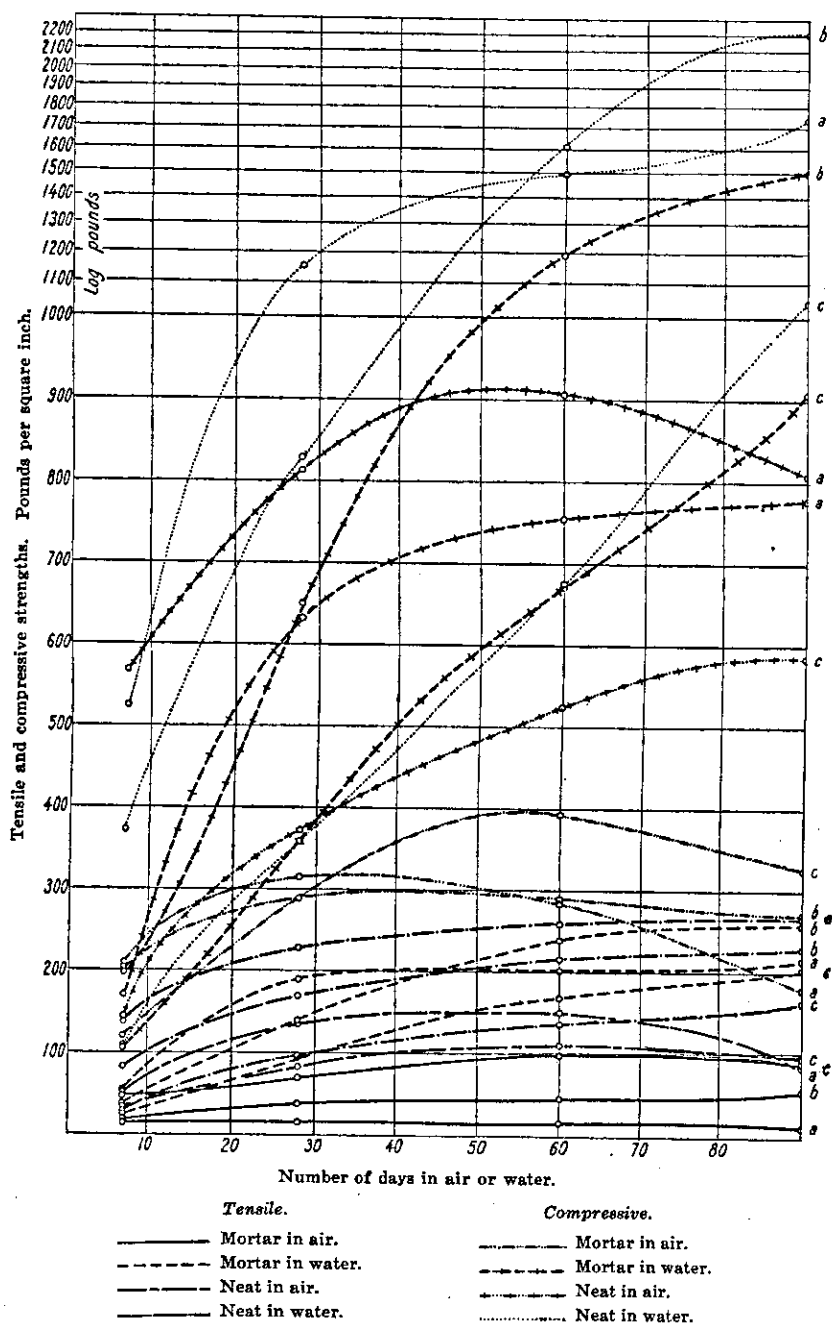


Fig. 1. Curves showing tensile and compressive strengths of volcanic tuff cement.

TABLE VII.—*Showing pozzuolanic properties of Meycauayan tuff when mixed with hydrated lime.*

30

Mixture No.	Specific grav-ity.	Time of set-ting.	Parts by weight.		Fineness.		TENSILE STRENGTH IN POUNDS PER SQUARE INCH.															
			Tuff.	Hy-dra-ted lime.	Through 200 mesh.	Through 100 mesh.	Neat in air.				Neat in water.				1 : 3 mortar in air.				1 : 3 mortar in water.			
							7 days.	28 days.	60 days.	90 days.	7 days.	28 days.	60 days.	90 days.	7 days.	28 days.	60 days.	90 days.	7 days.	28 days.	60 days.	90 days.
A-----	2.52	25	90	10	81.2	95.6	49	133	154	84	138	227	251	267	13	15	15	11	54	189	205	215
B-----	2.51	165	75	25	83	96	72	(*)	99	(*)	82	168	214	229	18	37	45	56	38	138	240	257
C-----	2.43	237	50	50	79	94.6	33	82	110	95	29	96	137	163	47	69	97	90	22	92	168	204
TENSILE STRENGTH IN KILOS PER SQUARE CENTIMETER.																						
A-----	2.52	25	90	10	81.2	95.6	3.44	9.35	10.83	5.90	9.70	15.96	17.65	18.77	0.914	1.05	1.05	0.774	3.79	13.29	14.41	15.2
B-----	2.51	165	75	25	83	96	5.06	(*)	6.96	(*)	5.76	11.81	15.05	16.10	1.27	2.60	3.16	3.94	2.67	9.70	16.88	18.07
C-----	2.43	237	50	50	79	94.6	2.32	5.76	7.73	6.68	2.04	6.75	9.63	11.46	3.31	4.85	6.82	6.33	1.54	6.47	11.82	14.34
COMPRESSIVE STRENGTH IN POUNDS PER SQUARE INCH.																						
A-----	2.52	25	90	10	81.2	95.6	568	812	906	808	524	1,152	1,497	1,734	209	313	283	179	170	631	753	778
B-----	2.51	165	75	25	83	96	354	682	635	678	371	828	1,612	2,202	203	288	289	269	198	649	1,187	1,498
C-----	2.43	237	50	50	79	94.6	144	372	523	586	105	356	675	1,043	120	314	393	326	108	358	672	906
COMPRESSIVE STRENGTH IN KILOS PER SQUARE CENTIMETER.																						
A-----	2.52	25	90	10	81.2	95.6	39.94	57.10	63.71	56.82	36.84	81.01	105.28	121.91	14.69	22.01	19.90	12.59	11.95	44.37	52.95	54.71
B-----	2.51	165	75	25	83	96	24.89	47.96	44.65	47.67	26.09	58.22	113.36	154.82	14.27	20.25	20.32	18.91	13.92	45.64	83.47	105.34
C-----	2.43	237	50	50	79	94.6	10.12	26.16	36.77	41.21	7.38	25.03	47.46	73.39	8.43	22.08	27.63	22.92	7.59	25.17	47.25	63.71

\* All cracked.

until they possess sufficient cohesion to stand handling, and then store them for the remaining time in water. The results thus obtained are supposed to indicate the behavior of the material when used in construction. In practice, however, the concrete is sometimes kept moist for a time by covering with damp cloths and afterward sprinkling occasionally with water. At other times, and this is the usual practice, the work is not kept covered with wet cloth or earth, but is simply allowed to dry under the influence of the sun and air currents. It is rarely totally immersed in water. Laboratory tests should be made as nearly as possible in conformity with construction practice. In order to note the effect of air storage equivalent to ordinary construction practice on the tuff mixtures, one half of the test specimens was stored in air, the other half was kept in fresh water, up to the time of testing. The results obtained on the specimens stored in air are altogether different from those obtained on specimens kept in water, as shown in Table VII and fig. 1. It would be interesting to conduct similar experiments upon Portland cement mortars. Tensile and compressive tests were made at the end of seven, twenty-eight, sixty, and ninety days. The briquettes, both mortar and neat, were broken in a standard Fairbanks testing machine. Compression tests were made on a four-screw Olsen testing machine, having a capacity of thirty thousand pounds.

#### CONCERNING TEST SPECIMENS

For the purpose of carrying out this investigation, a set of 30 cast-iron cylindrical compression molds having a diameter of 3.568 inches (9.063 centimeters) and a height of 7.136 inches (18.125 centimeters) were specially made. The diameter was made 3.568 inches so that the area of the bearing faces would be exactly 10 square inches (64.514 square centimeters); this greatly facilitates the calculation of the strength per square inch and is a very desirable feature when a considerable number of determinations are made. The height was made twice the least lateral diameter in order to secure the correct shearing angle during rupture.

Bauschinger<sup>14</sup> has shown that the following equation holds true for sandstone and similar substances.<sup>15</sup> The equation show-

<sup>14</sup>Johnson, J. B., *The Materials of Construction*. John Wiley & Sons, New York (1912), 31.

<sup>15</sup>In my opinion this equation is applicable to the tuff mixtures under study; at least, a few comparative tests, using cubical and cylindrical speci-

ing the relation between the strength of a prism to the strength of a cube, using Bauschinger's data, is

$$\frac{\text{strength of prism}}{\text{strength of cube}} = 0.778 \text{ plus } 0.222 \frac{d}{h}$$

in which  $d$  equals the least lateral diameter and  $h$  equals the height of the prism. The equation shows that the strength of a prism having a height twice as great as its least lateral diameter is only 88.9 per cent of that shown by a cube. Cubes are very generally used in making compressive tests, but their use is not to be recommended. Not only do they give results that are too high in calculating the factor of safety, but since the theoretical angle of rupture approaches  $60^\circ$  and not  $45^\circ$ , as was formerly thought to be the case, it is apparent that the ratio between the height and the least lateral dimension  $\left(\frac{h}{d}\right)$

should have a minimum of not less than 1.5, so that failure may proceed along the normal angle. Bauschinger has made a very careful and detailed study of this problem,<sup>19</sup> and the conclusions cited are inferred from data obtained during the investigation of a uniformly fine-textured sandstone.

A cylindrical specimen possesses a very desirable feature over a cubical one in that there is an absence of the numerous edges and sharp corners characteristic of the cube. With cylindrical specimens, molding operations are simplified, there is less danger of getting a defective test piece, and, finally, there is less possibility of injury during manipulation.

#### CHARACTERISTICS OF MATERIAL

In this investigation three or four compression specimens were made for each test; the results shown in the table were obtained by taking the average of at least three breaks. In the tensile tests a minimum of eleven briquettes were broken at each test; in some instances, seventeen. As was to be expected, the compression results were much more uniform than the

mens with the height twice the least lateral diameter, gave results that fitted the equation. The cylindrical shape with  $\frac{d}{h} = \frac{1}{2}$  gave strengths varying from 60 per cent to 80 per cent of the strengths shown by the cubical specimens. Not enough tests were made to calculate an accurate constant for this tuff, but the results obtained were sufficiently significant to indicate that Bauschinger's equation is applicable.

<sup>19</sup> Bauschinger, J., *Mitt. a. d. Mech. Tech. Lab. d. k. Tech. Hochschule, Muenchen* (1876), 6.

tensile strength. Great variation was noticed between the strengths of briquettes in the same lot; this was especially true of the briquettes stored in air. I attribute this variation to shrinkage cracks set up by unequal rates of drying and to fine grinding; in part it is characteristic of this kind of cementing material.

Before tempering the various mixtures, the normal consistency of each was determined by the ball method. Mix A required 35 per cent of water; mix B, 36 per cent; and mix C, 36 per cent.

The quantity of material mixed at one time was of such bulk as to prohibit working directly with the hands. For the neat batches about 65 kilograms of the cement were weighed out and formed into the shape of a cone with a crater in the center. The mixing was done upon a concrete surface. Water was poured into the crater and the mass thoroughly mixed for twenty minutes by three assistants using shovels. The work of mixing was laborious on account of the sticky nature of the paste. It adhered tenaciously to the shovels, somewhat like stiff clay, and had a tendency to ball up into separate lumps. During the molding process considerable tamping was necessary to make the cement coalesce. Especial care had to be taken to tamp the paste into the molds in order to reduce the air bubbles and voids to a minimum; even with the care taken, some of the specimens contained excessive voids, which in part account for the variation in some of the results obtained. The mortar mixtures worked much more easily and produced better specimens. More water would make the operation of mixing less laborious, but the additional amount added would cause undue shrinkage of the air specimens and thus lead to serious cracks which would make the specimens worthless. In fact all specimens showed more or less shrinkage. No measurements were made, but shrinkage was easily noticeable twenty-four hours after the specimens had been made and allowed to stand in the air. Some of the briquettes of mix B stored in air were cracked into several pieces by shrinkage, and therefore no results were obtained for these periods. Some of the neat compressive specimens stored in air were also slightly cracked on the surface through the same cause. All neat specimens stored in air showed a tendency to develop hair cracks; the troweled surface of these specimens flaked or peeled off, exposing a rough undersurface. This tendency was not noticed in the mortar specimens. The addition of sand reduced the shrinkage considerably.

## SUMMARY

Three mixtures of Meycauayan tuff with hydrated lime were made and subjected to a number of physical tests. Mix A contained 90 per cent tuff; B, 75 per cent; and C, 50 per cent. The following conclusions are based on the results obtained:

1. A mixture of Meycauayan tuff and hydrated lime possesses hydraulic properties. It is not suitable for construction permanently exposed to the air, but develops considerable strength in water.

2. Increasing percentage of lime is accompanied by a retardation of set and a decrease in the specific gravity.

3. The tensile strength is influenced by the fineness of the material. A coarser grind shows lower tensile strength, but the specimens are less liable to crack when stored in air.

4. In general, mix B gave the most satisfactory results.

## ILLUSTRATION

### TEXT FIGURE

FIG. 1. Curves showing tensile and compressive strengths of volcanic tuff cement.

## THE OXYGEN-CONSUMING POWER OF NATURAL WATERS \*

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Although the determination of the oxygen-consuming capacity of a water as measured by its ability to reduce potassium permanganate is known to have marked limitations, there can be little question that a series of determinations at regular intervals is of great value in determining the quality of a water supply, especially when studied in conjunction with bacteriological data.<sup>1</sup> The oxygen-consuming capacity is a sensitive index of the fluctuation in the quality in a water supply, and it is especially valuable because it shows relatively small differences rapidly and with some degree of accuracy.

Many methods for measuring the oxygen-consuming power have been proposed and discussed, among them are the determination in acid solution after digestion with potassium permanganate at boiling temperature (Kubel method), the digestion with permanganate in alkaline solution (Schulze method),<sup>2</sup> the digestion with acid permanganate at room temperature or at even lower temperatures,<sup>3</sup> and the digestion with alkaline permanganate solution at reduced temperatures.<sup>4</sup> No less than six different procedures for digestion and titration of samples are recorded by the American Public Health Association.<sup>5</sup> As very slight modifications in method lead to great discrepancies in results, it becomes of interest to study the various procedures, with a view to comparing the results obtained by different methods, as well as for the purpose of studying the factors influencing the determination.

That the oxygen consumption is not a reliable measure of the organic matter in water has repeatedly been pointed out.<sup>6</sup> Tie-mann and Preusse,<sup>7</sup> in experiments with various substances such as tartaric acid, cane sugar, asparagin, aniline hydrochloride, and the like, found that the oxidation by means of permanganate was usually less than the value corresponding to the

\* Received for publication December 8, 1915.

<sup>1</sup> Barnard, *Eng. Rec.* (1913), 68, 297.

<sup>2</sup> *Dingler's polytech. Journ.* (1868), 188, 197.

<sup>3</sup> Dupré, *Analyst* (1886), 10, 188.

<sup>4</sup> Winkler, *Zeitschr. f. analyt. Chem.* (1914), 53, 561.

<sup>5</sup> Standard Methods of Water Analysis, 2d ed. New York (1912), 28.

<sup>6</sup> Flugge, *Hygienische Untersuchungsmethoden*. Veit & Co., Leipzig (1881), 244.

<sup>7</sup> *Ber. d. deutsch. Chem. Ges.* (1879) (II), 12, 1906.

known content of organic matter, in some cases (benzoic acid) there was little or (for urea) no action whatever. Cavel,<sup>8</sup> working with known concentrations of various organic substances, including alcohols, aldehydes, acids, ketones, amides, phenols, sugars, indole, urea, skatole, etc., came to the conclusion that the determination as applied to water gave no indication of the nature or quantity of organic matter present.

The determination of oxygen consumed not only fails to measure accurately the amount or kind of organic matter present, but it is also greatly affected by the presence of different foreign substances. Unoxidized mineral substances, such as ferrous salts, sulphides, and nitrites,<sup>9</sup> introduce errors which it is generally sought to overcome by digesting the sample for three minutes in the cold with sulphuric acid and direct titration with permanganate. M. Dittrich<sup>10</sup> recommends that any sulphur in water should be precipitated before the regular procedure for oxygen consumption is begun.

As early as 1886, Dupré<sup>11</sup> called attention to the fact that a high content of soluble chlorides greatly affected the oxygen-consuming capacity when the digestion was made at boiling temperature, owing to the decomposition of the permanganate in the presence of sulphuric acid and chlorides, chlorine being set free. He found that as little as 15 parts per million of chlorine (1.05 grains per gallon) would appreciably affect the results. It is probably due to his work that, in the English standard methods,<sup>12</sup> digestion is carried on at 27° C. (80° F.), a correspondingly longer digestion period being used than when digestion is carried on at boiling temperature.

In short, the determination of the oxygen-consuming capacity gives comparable results only when a fixed method is strictly adhered to, and even in this case certain errors may creep in which go far toward destroying the value of the analysis.

We have attempted to study quantitatively some of the factors which influence the determinations. All the data recorded are the average of two or more concordant determinations. Duplicate titrations which did not check each other within 0.5 cubic centimeter were rejected.

<sup>8</sup> *Rev. gen. Chem.* (1912), 15, 73.

<sup>9</sup> *Standard Methods of Water Analysis*, 2d ed. Am. Pub. Health Assoc., New York (1912) 28.

<sup>10</sup> *Zeitschr. f. analyt. Chem.* (1912), 50, 697.

<sup>11</sup> *Analyst* (1886), 10, 188.

<sup>12</sup> Cf. Sutton, *Volumetric Analysis*, 10th ed. P. Blakiston's Son & Co., Philadelphia (1911), 485.

EFFECT OF TIME OF DIGESTION

A sample of river water (from the reservoir of the city of Manila) containing less than 5 parts per million of chlorides was used for these determinations. The oxygen-consuming capacity was determined practically as outlined by the American Public Health Association<sup>13</sup> by adding 10 cubic centimeters of dilute (1:3) sulphuric acid and 10 cubic centimeters of potassium permanganate (1 cubic centimeter=0.1 milligram oxygen) to 200 cubic centimeter samples of water in the cold and digesting for varying periods in a boiling-water bath. After digestion, 10 cubic centimeters of oxalic acid were added, and the sample was titrated at boiling temperature with permanganate.

The analytical results are recorded in Table I.

TABLE I.—*Effect of time of digestion on the determination of the oxygen-consuming capacity.*

[Temperature of digestion, 100° C.]

Time.	Permanganate required.	Oxygen consumption (parts per million).
<i>Min.</i>	<i>cc.</i>	
0	0.82	0.35
15	1.10	0.49
30	1.27	0.57
45	1.29	0.58
60	1.34	0.61
120	1.75	0.81
240	2.46	1.16

The decomposition showed no signs of reaching an end point, and proceeded regularly, although at the end of a four-hour digestion the volume of the sample was greatly reduced. The time of digestion is, therefore, a very important factor, and strict adherence to a fixed digestion period is necessary to ensure concordant results.

With digestion at room temperature, the effect, although less marked, is still appreciable, as shown by Table II.

TABLE II.—*Effect of time of digestion on oxygen consumption.*

[Temperature of digestion, 23° C.]

Hours.	Oxygen consumption. (Parts per million.)
2	0.60
4	0.64
6	0.68
8	0.69
24	0.74

<sup>13</sup> Op. cit., 27.

Even at 10° C. the effect is still marked, although in this case the difference between four- and eight-hour digestion is negligible for practical purposes. An end point is apparently reached after about seven hours, as is shown by the data in Table III.

TABLE III.—*Effect of time of digestion on oxygen consumption.*

[Temperature of digestion, 10° C.]	
Hours.	Oxygen consumption. (Parts per million.)
2	0.63
4	0.66
6	0.67
8	0.71
24	0.71

In digestion at or below room temperature with the method described above, the oxygen consumed is the summation of that used up during the digestion period and that required during the time the sample is being heated to boiling temperature. The latter amount is far from negligible; hence better results are obtained by titrating the excess of potassium permanganate in the cold with sodium thiosulphate, using potassium iodide and starch indicator, than are obtained by adding an excess of oxalic acid and titrating back with permanganate at boiling temperature. The difference in results is shown in Table IV.

The fact that no definite end point is attained, except perhaps at low temperature, seems to show that great concordance need not be expected when the digestion is carried on at different temperatures. The discrepancy in results is indicated by the data in Table IV.

TABLE IV.—*Effect of temperature and method of titration on oxygen-consuming capacity.*

Temperature of digestion.	Time.	Oxygen consumed (parts per million).	
		Cold titration with thiosulphate.	Hot titration with oxalic acid and permanganate.
°C.	Hours.		
10	24	0.34	0.62
28	4	0.55	0.64
100	0.5	-----	0.79
100	(*)	-----	0.5

\* Just heated to boiling.

### EFFECT OF CHLORIDES

As chlorides have a marked effect on permanganate digestion at boiling temperature, and as the typical Philippine waters submitted to this laboratory for analysis are generally high in chlorine, it seemed worth while to us to make accurate measurements on waters of varying chloride content.

The determinations were made with the ordinary distilled water of the laboratory, a water which still contained a small amount of organic matter. The same water was used in making up a standard solution of fused sodium chloride, portions of which were then diluted with varying amounts of water to give samples of the desired concentrations. The determinations of oxygen consumption were made in the usual manner, using 100 cubic centimeter samples and digesting at 100° C. for thirty minutes.

The analytical results are recorded in Table V.

TABLE V.—*Effect of dissolved chlorides on determinations of oxygen-consuming capacity.*

[Sample, 100 cubic centimeters; digested for thirty minutes at 100° C.]

#### SERIES 1.

Chlorine content (parts per million).	Permanganate required.	Difference in permanganate required.	Error introduced in terms of oxygen consumed (parts per million).
	cc.	cc.	
0	1.14		
5	1.20	0.06	0.01
10	1.22	0.08	0.03
20	1.33	0.19	0.14
50	1.36	0.22	0.17
100	1.40	0.26	0.21

#### SERIES 2.

0.0	0.56		
43.3	0.73	0.17	0.16
65.0	0.85	0.29	0.27
77.0	0.85	0.29	0.27
93.4	0.94	0.38	0.37
118.3	1.02	0.46	0.44
161.0	1.10	0.54	0.52
197.0	0.90	0.34	0.32
253.0	1.13	0.57	0.55
355.0	1.32	0.76	0.73
442.5	1.97	1.41	1.37
522.0	1.78	1.22	1.20
710.0	2.07	1.51	1.49
887.5	3.62	3.06	2.99
1,183.0	4.80	4.24	4.14
1,775.0	4.70	4.14	4.05
3,550.0	7.11	6.55	6.41

When the concentration of salt increased beyond  $250\pm$ , it became difficult to obtain concordant results, as the reaction then appeared to be far from equilibrium at the end of the half-hour digestion period.

It is clear from the data presented that the analysis will give concordant, comparable results only when the chlorine content is extremely low. As little as 5 parts per million introduce an appreciable error, while 50 parts per million, according to our results, will cause a decomposition of permanganate corresponding, in a 100 cubic centimeter sample, to an increase of 0.2 part per million in oxygen-consuming capacity.

It is interesting to note that the method of digesting at room temperature does not overcome the errors noted. Indeed Dupré<sup>14</sup> had already pointed this out and recommended that the digestion be carried on at a temperature as near  $0^{\circ}$  C. as possible. We conducted a series of digestions at room temperature ( $30^{\circ}$  C.) over four hours and obtained the results shown in Table VI.

TABLE VI.—*Effect of dissolved chlorides on the determinations of the oxygen-consuming capacity.*

[Sample, 100 cubic centimeters; digested for four hours at  $30^{\circ}$  C.]

SERIES 1.

Chlorine content (parts per million).	Permanganate required.	Difference in permanganate required.	Error introduced in terms of oxygen consumed (parts per million).
	cc.	cc.	
0	1.31		
5	1.33	0.07	0.07
10	1.46	0.15	0.15
20	1.48	0.17	0.17

SERIES 2.

[Twenty-four hours digestion period.]

0	0.73		
253	0.80	0.07	0.06
355	0.88	0.15	0.14
442.5	1.00	0.27	0.26
591	1.18	0.45	0.44
837.5	1.31	0.58	0.56
1,183	1.62	0.89	0.87
1,775	2.50	1.77	1.73
3,550	3.93	3.20	3.13

<sup>14</sup> *Analyst* (1886), 10, 188.

In these series the odor of chlorine could be plainly detected during digestion with permanganate and sulphuric acid in the samples containing over 10 parts per million of chlorides. The results, although lacking somewhat in uniformity, showed that an appreciable error is introduced even at 30° if the final titration is made at boiling temperature.

At 10° C. the error, although slighter, is still appreciable, as is shown by the data in Table VII.

TABLE VII.—*Effect of chlorides on the oxygen-consuming capacity.*

[Temperature of digestion, 10° C.]

Chlorine content (parts per million).	Permanganate required.	Error introduced in terms of oxygen consumed (parts per million).
	cc.	
0	11.43	0.0
10	11.50	0.03
100	11.50	0.03
250	11.61	0.09
1,000	12.98	0.8

Only part of the error can be ascribed to interaction of the permanganate and chlorides during digestion, as this reaction goes on at greatly accelerated speed while the sample is being heated to boiling; in fact, the amount of permanganate reduced during digestion at low temperature, although not negligible, is small as compared with that reduced during the short heating period. It is, therefore, possible to eliminate to some extent the error due to chlorides by performing the digestion at a moderate temperature (preferably below 15° C.) and titrating the excess of permanganate with sodium thiosulphate in the presence of potassium iodide and starch indicator. This is shown by the data in Table VIII.

TABLE VIII.—*Effect of chlorides on titration methods.*

Temperature of digestion.	Time of digestion.	Chlorine content (parts per million).	Oxygen consumed (parts per million).	
			Cold titration with thiosulphate.	Hot titration with permanganate.
°C.	Hrs.			
10	24	0	0.34	0.62
10	24	1,000	0.78	1.53
28	4	0	0.55	0.64
28	4	1,000	0.72	1.03

It is evident that the error due to the presence of chlorides persists even when digestion is carried on at moderate temperatures. In order to eliminate this error, digestion should be carried on in alkaline solution according to the method of Shulze or Winkler.<sup>15</sup>

Even in alkaline solution the presence of chlorides may introduce discrepancies. After digestion, when the solution is acidified before the addition of potassium iodide and titration with thiosulphate, sufficient chlorine may be liberated seriously to affect the results. With a chlorine content as high as 250 parts per million no serious error could be detected; with a chlorine content of 1,000 parts per million the discrepancy was appreciable.

A further error is caused by the actual reduction of potassium permanganate to potassium manganate in the presence of chlorides in alkaline solution, even when digestion is carried on at room temperature (30°C.). This was clearly indicated in a series of 24-hour digestions carried on at room temperature in alkaline solution by the change in color from red to green in the samples containing much salt.

A large number of experiments have been performed on digestions with alkaline solutions, but their results were not sufficiently conclusive to warrant their being included in this paper. As might be expected, the results obtained in alkaline solution are highly dependent on the concentration of alkali and on the temperature and time of digestion, so that comparable results can be obtained only by adhering to fixed procedure.

#### EFFECT OF HYPOCHLORITES

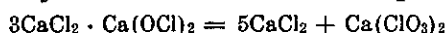
In studying the daily variation in oxygen consumption of a municipal supply, certain discrepancies were noted which induced us further to study the effect of hypochlorites or "free chlorine" on the amount of oxygen consumed. Glaser<sup>16</sup> states that through the addition of chloride of lime the oxygen consumption is first increased, because more organic matter is brought into solution—that is, into a more rapidly oxidizable form. After that a reduction in the required quantity of permanganate occurs, owing to the oxidation of organic material by the chloride of lime itself. He believes that the initial increase in oxygen consumption could not be ascribed to inter-

<sup>15</sup> *Dingler's polytech. Journ.* (1868), 188, 197; *Zeitschr. f. analyt. Chem.* (1914), 53, 561.

<sup>16</sup> *Arch. f. Hyg.* (1913), 77, 268.

action between hypochlorite and potassium permanganate in acid solution.

The presence of hypochlorites introduces an error in addition to, and opposite in sign from, the one caused by an increased chloride content. In hot digestion the hypochlorite changes to chlorate,<sup>17</sup> probably in accordance with the equation



and reacts with the organic matter present or with the oxalic acid generally used for titration purposes. The amount of permanganate required is, therefore, reduced, and a low oxygen consumption is recorded.

When chloride of lime is added to a water of known organic content, the oxygen consumption as determined by the standard method is invariably low, even when digestion is performed at room temperature (the sample being brought to boiling at the end of the digestion period and titrated in the regular way). This is clearly shown by the results of the following experiments:

TABLE IX.—*Effect of hypochlorites on oxygen consumption.*

SERIES 1.

[Distilled water, 200 cubic centimeter samples, digested thirty minutes at 100° C. with a standard permanganate solution, decolorized with standard oxalic acid solution, and titrated with permanganate at boiling temperature.]

	Available chlorine (parts per million).	Permanganate required.	Error involved in terms of oxygen consumed (parts per million).
		cc.	
Sample A.....	0	10.45	0
	1.75	10.15	0.15
	4.3	9.45	0.5
	17.5	8.8	0.8
Sample B.....	0	10.8	0
	5	10.1	0.3
	10	9.7	0.5

SERIES 2.

[River water treated as in series 1.]

Available chlorine added (parts per million).	Permanganate required.	Errors involved in terms of oxygen consumed (parts per million).
	cc.	
0	12.0	0
0.5	11.6	0.2
1.0	11.6	0.2

<sup>17</sup> Bhaduri, *Zeitschr. f. anorg. Chem.* (1897), 13, 385.

The following data were secured when samples were digested in the cold:

TABLE X.—*Effect of digestion at room temperature.*

[Distilled water, 200 cubic centimeter samples, digested four hours at 30° C., titrated hot.]

Available chlorine added (parts per million).	Permanganate required.	Errors involved in terms of the oxygen-consuming power (parts per million).
	cc.	
0	10.55	0
5	9.25	0.65
10	8.6	1.0

The errors recorded in this last series are of the same order of magnitude as those previously mentioned (Table IX); hence the action of hypochlorite on organic matter proceeds at moderate temperature as well as at high temperature.

That the hypochlorite reacts with the organic matter and that its effect can be only partially eliminated by boiling with sulphuric acid according to the equations

$\text{CaCl}_2 \cdot \text{Ca}(\text{OCl})_2 + 2\text{H}_2\text{SO}_4 = 2\text{CaSO}_4 + 4\text{HCl} + 2\text{O}$  and  $4\text{HCl} + 2\text{O} \rightleftharpoons 2\text{H}_2\text{O} + 4\text{Cl}$  are indicated by the following data, which resulted on boiling chlorinated samples with sulphuric acid for fifteen minutes before digesting with permanganate:

TABLE XI.—*Effect of boiling with sulphuric acid in presence of hypochlorites.*

Available chlorine added (parts per million).	Permanganate required.	Errors involved in terms of the oxygen-consuming power (parts per million).
	cc.	
0.0	11.9	0.0
2.0	11.1	0.4
8.0	10.9	0.5
0.0	10.4	0.0
8.0	8.0	2.4
0.0	12.0	0.0
1.0	11.6	0.2

The hypochlorite changes partially to chlorate even in acid solution at boiling temperature. Thus a hypochlorite solution equivalent to 5 milligrams of available chlorine, boiled with sulphuric acid for five minutes, still had the power to oxidize 0.9 milligram of oxalic acid.

Obviously, then, the presence of hypochlorites in appreciable quantities introduces errors into the determination of oxygen consumption, although this determination is at best so notoriously inaccurate that the error introduced by free chlorine is generally of minor importance unless great accuracy is desired. The effect of hypochlorites can readily be eliminated by the addition of a few milligrams of sodium sulphite. After a few hours the excess sodium sulphite is decomposed and it has no appreciable effect on the determination. Before proceeding to the final digestion, however, it is best to digest the sample, which has been standing in contact with sodium sulphite, for three minutes with sulphuric acid, in the cold, and to add a drop of permanganate to make sure that the sulphite has all been destroyed.

#### SUMMARY AND CONCLUSIONS

Some of the factors influencing the determination of the oxygen-consuming capacity by means of potassium permanganate in acid solution have been studied quantitatively. Time and temperature have so great an effect that concordant results cannot be obtained unless great care is exercised to have all determinations made under identical conditions.

The influence of dissolved substances, especially of chlorides, is very large. The effect of the latter is reduced, although not eliminated, if digestion is carried on at or below room temperature. The final titration of excess potassium permanganate should be made with sodium thiosulphate (in the presence of potassium iodide and starch indicator). The error due to chlorides is reduced by digesting the water samples with potassium permanganate in alkaline (Schulze method), instead of in acid solution, the final titration being made with sodium thiosulphate.

Hypochlorites oxidize organic matter in cold or hot solution and should be eliminated before a determination of the oxygen-consuming power is made.

The determination of oxygen consumption at best is not an accurate measure of the organic content of a water, and it gives such uncertain results that isolated determinations are of very little value. It is only when a water supply is to be examined repeatedly that the determination becomes very useful.

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